(11) (A) No. 1,106,557

(45) ISSUED 810811

(52) CLASS 9-26

(51) INT. CL.[2] D21C 3/00

(19) (CA) **CANADIAN PATENT** (12)

(54) PROCESS FOR PRODUCTION OF PULP

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(21) APPLICATION No. 292,069

(22) FILED 771130

(30) PRIORITY DATE Japan (148492/1976) 761210

No. OF CLAIMS 18 - NO DRAWING

PROCESS FOR PRODUCTION OF PULP

Abstract of the Disclosure:

An improved process for the production of pulp characterized by the employment of a novel type of cooking aid is disclosed. The cooking is carried out in the presence of a small amount of a compound selected from the group consisting of hydroxyanthracenes and derivatives thereof. The cooking yield is substantially increased and the quality of the resulting pulp and paper is improved.

This invention relates to a process for the production of pulp. More particularly, the invention relates to a process for the production of pulp from lignocellulosic materials by carrying out the cooking in the presence of a small amount of a novel type of cooking aid selected from the group consisting of hydroxyanthracenes and derivatives thereof. The cooking aid can be added to a cooking liquor in any of the conventional alkaline, or sulfite or the like cooking processes. The term "alkaline cooking process" or simply "alkaline process" herein used includes various alkaline cooking processes such as a kraft process, a soda process, a sodium carbonate process and the like. Similarly, the term "sulfite cooking process" or simply "sulfite process" herein used includes various sulfite cooking processes such as an alkaline sulfite process, a neutral sulfite process, a bisulfite process, and the like.

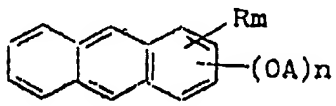
In the field of producing pulp from lignocellulosic material such as wood, bagasse, hemp and the like, a number of various trials have been repeated from old times to improve the cooking yield, the rate of cooking and the quality of the product pulp, aiming at the economical production of good quality pulp with decreased consumption of raw material and of energy. For example, instead of an ordinary kraft process in which lignocellulosic material such as wood is subjected to treatment by a cooking liquor comprising essentially sodium hydrate and sodium sulfide, a modified process thereof which is usually called a "polysulfide process" and is characterized by being subjected to treatment with a cooking liquor comprising a sodium polysulfide is nowadays more popularly employed. Various other modifications, for example, the addition of

borohydride, hydrazine, hydroxylamine or the like have also been proposed and tried. Most of such modified processes, however, have not been fit for practical use because in some cases total or partial change of the processing equipment is required, in other cases there is a significant increase in production cost, and in other cases the process is not applicable to soft or hard woods or both. Thus, except for said polysulfide process, none of the above-mentioned prior art processes is more than a laboratory model.

Accordingly, the object of the present invention is to provide a novel process for the production of pulp completely free from the disadvantages mentioned above. The novel process of the present invention is characterized by the selective use of a specific type of a cooking aid comprising at least one member selected from the group consisting of hydroxyanthracenes and the derivatives thereof. More particularly, in one aspect of the present invention, there is provided a process for producing alkaline pulp by carrying out the cooking of lignocellulosic materials such as wood, bagasse, hemp and the like in an alkaline cooking liquor in the presence of a small amount of hydroxyanthracene or a derivative thereof which is added as a novel type of cooking aid. In another aspect of the present invention, there is provided a process for producing sulfite pulp by carrying out the cooking of said lignocellulosic materials in a cooking liquor comprising sulfite in the presence of a small amount of the same cooking aid as mentioned above. As a result of effecting the cooking of such lignocellulosic materials as mentioned above in the presence of a specific amount of said novel cooking aid according to the present invention, the solution velocity of lignin from said

lignocellulosic materials is substantially increased, and in turn the rate of cooking is substantially increased too. The cooking yield in pulp production is also substantially improved as compared with the prior art process using the same degree of cooking. This is because hydroxyanthracene or a derivative thereof added to the cooking liquor functions as a cooking aid to promote the dissolution of lignin into the cooking liquor as well as to prevent the degradation of cellulose and hemicellulose throughout the cooking treatment. As a result of using such a novel cooking aid, the cooking yield and also the quality of the resulting pulp are improved and the rate of cooking is increased. Incidental to the increased rate of cooking, the amounts of cooking chemicals and steam required for heating are also substantially reduced.

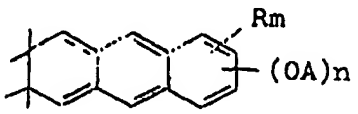
Typical compounds which can be advantageously employed as said cooking aid in the practice of the present invention include hydroxyanthracenes and derivatives thereof having the following general formula:



..... (1)

wherein R represents H, COOX wherein X is H or Na, or SO_3Y wherein Y is H or Na; A represents H or Na; m represents 0, 1 or 2; and n represents 1 or 2. The case wherein R represents H in the above general formula refers to a case in which at least one carbon atom in the anthracene nucleus loses its double bond to change from CH to CH_2 in the same position. Namely, the compounds defined by the above general formula (1) include those to be obtained by the addition of at least one hydrogen atom to the carbon atom in the anthracene nucleus

to have it lose its double bond and change from its CH form to CH_2 form in the same position, and include, for example, the compounds represented by the general formulas:



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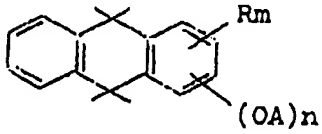


..... (3)

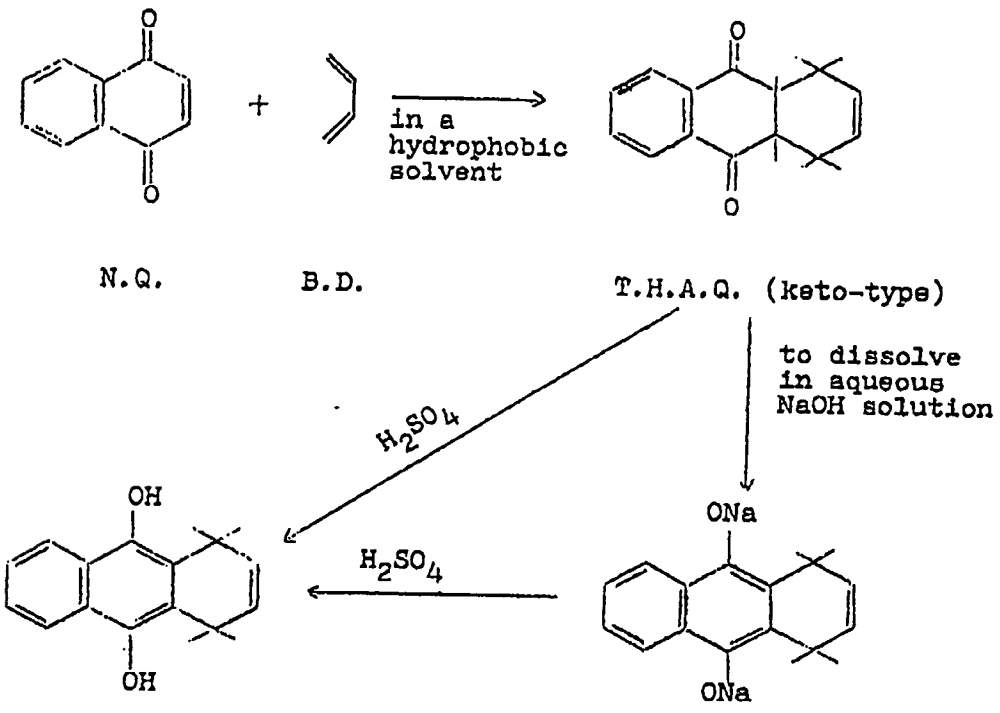
wherein R, A, m and n have the same meanings as already defined.

Among those compounds, dihydroxyanthracene, dihydroxydihydroanthracene, carboxydihydroxyanthracene as well as dihydroxyanthracenesulfonic acids including their sodium salts and dihydroxyanthracene carboxylic acids including their sodium salts can be most advantageously employed in the practice of the present invention.

These novel cooking aid compounds are preferably used in an amount in the region of 0.005 - 3% by weight based on the bone dry weight of the raw material chips or the lignocellulosic materials to be added to the cooking liquor. If the compound is used in an amount in the region of 0.01 - 0.1% by weight based on the same standard, optimum best results will be obtained.

Among compounds represented by the general formulas (1) - (3) the dihydrodihydroxyanthracene can easily be synthesized from naphthoquinone, and butadiene by making use of Diels-Alder reaction. For example, if naphthoquinone and butadiene are reacted with each other in a hydrophobic solvent such as chloronaphthalene in the known Diels-Alder

reaction as disclosed, for example, in U.S. Patent 2,938,913, tetrahydroanthraquinone is obtained according to the equation as shown below. This product changes, upon being dissolved in an aqueous alkaline solution such as an aqueous sodium hydroxide solution, to an alkali salt of dihydrodihydroxyanthracene, which can be treated with an acid such as sulfuric acid, hydrochloric acid or the like to precipitate dihydrodihydroxyanthracene. Alternatively, tetrahydroanthraquinone can directly be treated with an aqueous solution of an acid such as sulfuric acid to obtain dihydrodihydroxyanthracene as a precipitate as disclosed in USP 1,890,040, page 2, right column.



The cooking aid used in the present invention is easy to dissolve in the cooking liquor. In order to carry out the process of the present invention, no special change is required with respect to the cooking conditions except that a specified amount of said cooking aid is merely added to an ordinary cooking liquor. The following examples will illustrate the preferred embodiments of the present invention.

Example 1

600 g of softwood chips were placed in a 4-liter capacity autoclave, to which was added a kraft process cooking liquor having 17% active alkali and 25% sulfidity. Then, dihydroxydihydroanthracene prepared by the process as explained hereinbefore in an amount of 0.05% by weight based on the bone dry weight of the chips was added to the same cooking liquor and cooking was carried out at 165°C for 75 minutes.

For comparative purposes, the same experiment was repeated except that dihydroxydihydroanthracene was omitted. The results of these experiments were as shown in Table 1 below.

Table 1

	Kraft process cooking with dihydroxydihydro-anthracene (present invention)	Kraft process cooking without dihydroxydihydro-anthracene (prior art)
Cooking yield (%)	48.6	46.5
Kappa number	42	51
Burst Index*	6.9	6.2
Breaking length (km)	8.2	7.0
Tear factor	170	170

* determined by JIS P-8210 (Testing Method for Strength of Paper Pulp)

Example 2

700 g of hardwood chips were placed in a 4-liter capacity autoclave, to which a soda process cooking liquor having 15.5% (as Na_2O) caustic soda and dihydroxyanthracene in an amount of 0.02% by weight based on the bone dry weight of the chips was added and cooking was carried out at 155°C for 75 minutes.

Next, for comparative purposes, the same experiment was repeated except that dihydroxyanthracene was omitted. The results of these experiments are shown in Table 2 below.

Table 2

	Soda process cooking with dihydroxy-anthracene (present invention)	Soda process cooking without dihydroxy-anthracene (prior art)
Cooking yield (%)	53.9	53.0
Kappa number	50	78
Burst Index*	4.3	3.0
Breaking length (km)	6.1	4.5
Tear factor	110	100

* determined by JIS P-8210 (Testing Method for Strength of Paper Pulp)

Example 3

700 g of hardwood chips were placed in a 4-liter capacity autoclave, to which was added a sodium carbonate process cooking liquor containing 10% sodium carbonate and 0.1% by weight, based on the bone dry weight of the chips, of sodium dihydroxyanthracenecarboxylate and cooking was carried out at 180°C for 20 minutes. Then, the cooked chips were beaten by a disk refiner to a freeness of 450 cc.

For comparative purposes, the same experiment was repeated except that sodium dihydroxyanthracenecarboxylate was omitted. The results of these experiments are shown in Table 3 below.

Table 3

	Sodium carbonate process cooking with sodium dihydroxyanthracene-carboxylate (present invention)	Sodium carbonate process cooking without sodium dihydroxyanthracene-carboxylate (prior art)
Cooking yield (%)	82.0	78.9
Burst Index*	1.8	1.7
Breaking length (km)	3.2	2,5
Folds, double	20	14
Ring crush Resistance	14.2	13.5
Concora crush Resistance	19.5	19.0

* determined by JIS P-8210 (Testing Method for Strength of Paper Pulp)

Example 4

400 g of flax was placed in a 4-liter capacity autoclave, to which was added a cooking liquor containing 18% sodium sulfite and 3% caustic soda, both based on the weight of raw material, and sodium dihydroxyanthracenesulfonate in an amount of 0.05% based on the bone dry weight of the raw material and cooking was carried out at 180°C for 4 hours. Separately, for comparative purposes, the same experiment was repeated except that sodium dihydroxyanthracenesulfonate was omitted. The results of these experiments are shown in Table 4 below.

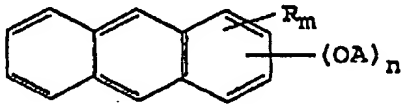
Table 4

	Sulfite cooking with sodium dihydroxy-anthracenesulfonate (present invention)	Sulfite cooking without sodium dihydroxy-anthracenesulfonate (prior art)
Cooking yield (%)	62.5	58.5
Kappa number	8	12
Breaking length (km)	8.9	7.6
Tear factor	190	170

The embodiments of the invention in which an exclusive property of privilege is claimed are defined as follows:

1. An improved cooking process for the production of pulp from lignocellulosic material comprising cooking lignocellulosic material in a cooking liquor,

the improvement comprising admixing in said cooking liquor an amount, sufficient to increase the cooking rate of said lignocellulosic material, of a cooking aid comprising at least one member selected from the group consisting of compounds having the formula:



wherein m is 0, 1 or 2, n is 1 or 2, R is COOA, SO_3A or H, and A is H or Na; providing that

when m is 1, R is at least one of COOA or SO_3A and R cannot attach to the middle ring;

when m is 0 or 2, R is H; and

when R is H and m is 2, two carbon atoms of the anthracene nucleus lose their double bonds, and each such carbon atom takes the form of CH_2 instead of CH, in which case one H of each CH_2 is not counted as an R and may be substituted by OA.

2. The process of claim 1, wherein said cooking aid is at least one member selected from the group consisting of dihydroxyanthracene, dihydroxydihydroanthracene, carboxydihydroxy-anthracene and dihydroxyanthracene sulfonate.

3. The process of claim 1 wherein said cooking aid is used in an amount of from about 0.005 to about 3% by weight based on the bone dry weight of lignocellulosic material.

4. The process of claim 1, wherein said cooking aid is used in an amount of from about 0.01 to about 0.1% by weight based on the bone dry weight of lignocellulosic material.

5. The process of claim 3, wherein said cooking aid is 1,4-dihydro-9,10-dihydroxyanthracene or its sodium salt.

6. The process of claim 3, wherein said cooking aid is 1-hydroxyanthracene or its sodium salt.

7. The process of claim 3, wherein said cooking aid is 9,10-dihydroxyanthracene or its sodium salt.

8. The process of claim 3, wherein said cooking aid is 2-hydroxyanthracene or its sodium salt.

9. The process of claim 3, wherein said cooking aid is 9-hydroxyanthracene or its sodium salt.

10. The process of claim 3, wherein said cooking aid is 9,10-dihydroanthranol or its sodium salt.

11. The process of claim 3, wherein said cooking aid is 1,2-dihydroxyanthracene or its sodium salt.

12. The process of claim 3, wherein said cooking aid is 2,3-dihydroxyanthracene or its sodium salt.

13. The process of claim 3, wherein said cooking aid is 2,6-dihydroxyanthracene or its sodium salt.

14. The process of claim 3, wherein said cooking aid is 9,10-dihydroanthracene-9,10-diol or its sodium salt.

15. The process of claim 3, wherein said cooking aid is 9,10-dihydroxyanthracene-2-carboxylic acid or its sodium salt.

16. The process of claim 3, wherein said cooking aid is 9,10-dihydroxyanthracene-1-sulphonic acid or its sodium salt.

17. The process of each of claims 1, 6 or 7, wherein said cooking liquor is an alkaline process cooking liquor.

18. The process of each of claims 1, 6 or 7, wherein said cooking liquor is a sulfite process cooking liquor.

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